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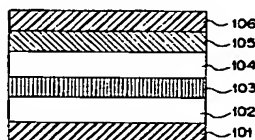
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**D-80336 München (DE)**(54) **Covering material for solar cell module.**

(57) A surface covering material for the solar cell module, excellent in transparency, scratch resistance, weather resistance and flame retarding property, is obtained by covering the outermost surface with trifluorochloroethylene-vinyl copolymer, and employing a hard film 105 in the surface covering material under trifluorochloroethylene-vinyl copolymer. The hard film 105 and trifluorochloroethylene-vinyl copolymer 106 are laminated and adhered with filler 104 to the photovoltaic element 103.

FIG. 1

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BACKGROUND OF THE INVENTIONField of the Invention

5 The present invention relates to a surface covering for a solar cell module in which photovoltaic element having a photoactive semiconductor layer serving as the photoelectric converting member is protected with resin, and more particularly a solar cell module capable of showing excellent performance even under external ambience.

10 Related Background Art

Among the recent worldspread consciousness for the ecological issues, the deepest concern is directed to the warning of the earth by CO<sub>2</sub> discharge, and the development and stable supply of clean energy are urgently wanted objectives. The solar cell is one of the most promising clean energy sources, because of  
 15 its safety and ease of handling. The solar cell has been proposed in various forms, such as (1) monocrystalline silicon solar cell; (2) polycrystalline silicon solar cell; (3) amorphous silicon solar cell; (4) copper-indium selenide solar cell; and (5) compound semiconductor solar cell. Among these forms, the thin film crystalline silicon solar cell, compound semiconductor solar cell and amorphous silicon solar cell are recent targets of active developmental works as they are relatively inexpensive and can be formed into a  
 20 large area.

Even among these cells, the amorphous (non-monocrystalline) solar cell, prepared by depositing silicon on a conductive metal substrate and forming a transparent conductive layer thereon is considered promising as the future module, as it is light in weight, excellent in impact resistance and rich in flexibility. However, different from the case of silicon deposition onto a glass substrate, the surface at the light  
 25 entrance side has to be coated with a transparent coating material in order to protect the solar cell.

Glass or resinous material of high weather resistance, such as fluorinated resin, has been employed for such surface coating material. Fig. 3 shows an example of such solar cell module, in which provided are a layer 304 of glass or resin of high weather resistance; a filler layer 303; a solar cell 302; and an insulating layer 301. The requirements for such coating material to be employed for surface protection of the solar cell  
 30 module include high weather resistance, high moisture resistance and high protecting ability.

In relation to the above-mentioned requirements for the coating material, the Japanese Patent Publication No. 4-76229 discloses, for a solar cell composed of a substrate and CdS/CdTe formed thereon, a protective film composed of a derivative of resin containing perfluoroalkylene radicals and active hydrogen atoms. Lumiflon (manufactured by Asahi Glass Co., Ltd.) is cited as an example of the resin containing  
 35 perfluoroalkylene radicals and active hydrogen atoms. According to the above-mentioned patent specification, Lumiflon is fluorine-containing polymer with a number-averaged molecular weight of 20,000 to 80,000, containing perfluoroalkylene radicals and pendant active hydrogen atoms, or more specifically OH radicals, and reacts with melamine or a compound containing isocyanate radicals to form crosslinked polymer, called derivative in said specification. The above-mentioned patent specification also discloses, in the description  
 40 of examples, the preparation of a protective film of high moisture resistance by crosslinking Lumiflon with an isocyanate or resol phenolic resin.

The coating film disclosed in the above-mentioned patent has to be positioned at the outermost surface of the solar cell module. The resin, after mixing with the crosslinking agent generally has a short pot life, which in practice has to be extended by protecting isocyanate with a blocking agent. Thus, if there is  
 45 intended a laminated structure in which a surfacial film is laminated on said resin, the crosslinking reaction may not proceed properly as the blocking agent cannot be liberated and evaporate. Also the lamination of the surfacial film after the crosslinking of resin is difficult because the crosslinked substance lacks adhesiveness or stickiness. Also any effective blocking agent is not known if melamine is employed as the crosslinking agent. For these reasons, the above-mentioned resin has to be used as the outermost surface  
 50 of the solar cell module. However, such resin has a low surface hardness, generally in the order of B to H in pencil hardness, and is easily scarred with sands and dusts present outdoors, and smear and dusts may be deposited on such scars to eventually intercept the solar light. Also such resin, if simply painted, tends to cause involvement of pinholes or dusts, giving rise to the introduction of moisture or oxygen to the photovoltaic element. Thus, there has not been known an organic surface coating material capable of  
 55 attaining weather resistance and moisture resistance at a high level.

Glass coating is best for preventing moisture absorption and yellow discoloration, and has therefore been employed frequently for sealing the solar cells. However such glass coating is defective in flexibility, impact strength, weight and cost.

Also the protective ability is important not only for maintaining the performance of the solar cell module itself but also securing the safety when the solar power generation becomes popular. The protective ability of the surface coating material can be tested with a "scratch test" in which, with a testing machine shown in Fig. 7, a steel blade is moved along the surface of the solar cell, with a speed of 152.4 mm/sec. and under a load of 907 g, and the solar cell passes this test if the electrical properties thereof show no defect in the electrical test thereafter.

The Japanese Patent Laid-open Application No. 59-56776 discloses a method of producing a solar cell module, featured by preparing a composite sheet consisting of a plastic sheet (or film) having a softening point of 120 °C or higher and having high optical transparency and a polyacrylic resin layer of a softening point of 120 °C or lower formed thereon, and either a polyacrylic resin sheet of a softening point of 120 °C or lower or a laminated sheet consisting of said resin sheet and a moisture preventing sheet, placing a solar cell element between said resin layers and applying heat and pressure to fuse or soften at least either of said acrylic resin layers thereby sealing said solar cell element. According to the specification of the above-mentioned patent, the plastic sheet (or film) can be composed of any plastic material having a softening point of 120 °C or higher and being optically transparent, but can be a sheet or a film of polycarbonate, polyamide resin, hard polyvinyl chloride resin or polyfluoroethylene resin. The recommended range of thickness is about 50 to 800  $\mu$ m. It is also disclosed that the surface of said sheet or film may be treated for example with silicon or magnesium fluoride in order to improve stress crack resistance.

However the weather resistance is still defective even by employing polycarbonate film as the hard film and silicone or magnesium fluoride as the surface coating material, because such surface coating material is incapable of intercepting the ultraviolet light which induces deterioration and discoloration of polycarbonate. For this reason there is no disclosure on the weather resistance of the hard film to be employed in the solar cell module.

For pressing these materials, there is usually employed the laminating method of superposing the surface covering material, the photovoltaic element and the rear covering material, with thermoplastic resin used as the filler layer 301, and heating these members under vacuum suction.

However, said surface covering material, if composed of glass, increases the weight and the cost though it can pass the scratch test mentioned above. On the other hand, fluorinated resin cannot pass the scratch test unless the filler is made thick enough, because the hardness of such fluorinated resin is low. Besides, if the filler is made thicker in order to pass the scratch test, the solar cell module may become combustible and unsuitable for use as the roofing material or the like. For resolving such drawbacks there should be employed a covering material of a higher hardness, instead of the fluorinated resin, but there has not been known, so far, any material having both the weather resistance and the water repellency and superior to fluorinated resin in performance.

### SUMMARY OF THE INVENTION

In consideration of the foregoing, the object of the present invention is to provide a surface covering material for the solar cell module, capable of minimizing the long-term deterioration of the performance thereof and ensuring improved safety thereof, thereby enabling inexpensive and stable supply of the solar cell module.

According to the present invention there is provided a solar cell module, provided with a photovoltaic element having at least a photoactive semiconductor layer as the photoelectric converting layer, featured by a fact that at least the outermost surface of the surface covering material at the light entrance side is composed of trifluorochloroethylene-vinyl copolymer.

The present invention provides following advantages:

- (1) Use of trifluorochloroethylene-vinyl copolymer at the outermost surface of the surface covering material at the light entrance side provides a surface covering material of excellent weather resistance. Use of the fluorinated resin in a portion of the solar cell module, requiring the highest weather resistance, ensures sufficient weather resistance at the outermost surface. Besides, different from other resins, trifluorochloroethylene-vinyl copolymer has mutual solubility with additive materials. Furthermore, because of the low film forming temperature, the organic additive materials evaporate or decompose less at the film forming operation. Consequently it is rendered possible to improve the weather resistance of the underlying covering material, by the addition of an ultraviolet absorber at the outermost surface. Furthermore, the low film forming temperature can reduce the thermal damage to the photo-voltaic element. More specifically, there can be reduced the influence to the conductive paste, solder etc. employed in the electrical connection of the photovoltaic element, whereby the weather resistance and reliability in repeated use can be improved;

(2) Lamination of the surface covering materials in the order of filler, hard film and trifluorochloroethylene-vinyl copolymer provides a surface covering material excellent in the scratch-resistant load. More specifically, a high scratch-resistant load can be ensured by the presence of the hard film as the intermediate material of the surface covering material. Also use of the filler excludes the gap in the surface covering material, even on a photovoltaic element with an irregular surface; and

(3) Addition of an inorganic ultraviolet absorber to trifluorochloroethylene-vinyl copolymer allows to retain the ultraviolet absorbing effect for a prolonged period, thereby ensuring long-term weather resistance of the covering material.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic cross-sectional view of a first embodiment of the solar cell module of the present invention;

Fig. 2 is a schematic cross-sectional view showing the basic configuration of a photovoltaic element, to be employed in the solar cell module shown in Fig. 1;

Fig. 3 is a schematic cross-sectional view of a conventional solar cell module;

Fig. 4 is a schematic cross-sectional view of an example of the covering of the solar cell module of the present invention;

Fig. 5 is a schematic cross-sectional view of a reference example 1 of the solar cell module;

Fig. 6 is a schematic cross-sectional view of another reference example of the solar cell module; and

Fig. 7 is a schematic view of a testing machine employed in the scratch test.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Fig. 1 schematically illustrates the configuration of a solar cell module of the present invention, composed of an insulator layer 101; a solar cell 103; fillers 102, 104; a hard film layer 105; and an outermost trifluorochloroethylene-vinyl copolymer layer 106. The light from outside enters from the outermost surface 106, then passes the hard film 105 and the filler 104, and reaches the solar cell 103 thereby generating electricity.

##### Rear Insulating Film 101

The rear insulating film 101 is provided for completing insulation in case of a photovoltaic element with conductive substrate, and can for example be composed of nylon, polyethylene, polyester or polystyrene.

##### Rear Filler 102

The filler to be used at the rear side is required to have adhesive power, weather resistance and ability for filling irregularities, but may be opaque. Examples of the material for said filler include fluorinated resin, ethylene-vinyl acetate copolymer (EVA), polyvinylbutyral (PVB), silicone resin, epoxy resin and acrylic resin.

Such resin may be added with a crosslinking agent, or an agent against thermal oxidation for improving heat resistance, or an ultraviolet absorber or an agent against photo-oxidation for improving photostability.

##### Photovoltaic Element 103

The photovoltaic element 103 of the present invention is preferably provided with a photoactive semiconductor layer, as the light converting member, on a conductive substrate. It is constructed, as schematically shown in Fig. 2, by a conductive substrate 201; a rear reflective layer 202; a photoactive semiconductor layer 203; a transparent conductive layer 204 and a current collecting electrode 205.

The conductive substrate 201 serves as the substrate for the photovoltaic element and also as a lower current-collecting electrode. It may be composed for example of silicon, tantalum, molybdenum, tungsten, stainless steel, aluminum, copper, titanium, a carbon sheet, a lead-plated steel plate, or a resinous film or a ceramic member bearing a conductive layer thereon.

On said conductive substrate 201, there may be formed, as the rear reflective layer 202, a metal layer and/or a metal oxide layer. The metal layer can be composed, for example, of Ti, Cr, Mo, W, Al, Ag or Ni, and the metal oxide layer can be composed, for example, of ZnO, TiO<sub>2</sub> or SnO<sub>2</sub>. Said metal layer and metal oxide layer can be formed, for example, by resistance-heated evaporation, electron beam evaporation or sputtering.

The photoactive semiconductor layer 203 is provided for effecting photoelectric conversion, and can be composed, for example, of polycrystalline silicon with pn junction, amorphous silicon with pin junction, or a compound semiconductor such as  $\text{CuInSe}_2$ ,  $\text{CuInS}_2$ , GaAs,  $\text{CdS/Cu}_2\text{S}$ ,  $\text{CdS/CdTe}$ ,  $\text{CdS/InP}$ , or  $\text{CdTe/Cu}_2\text{Te}$ . Said photoactive semiconductor layer can be formed, for example, by thermal treatment of an amorphous silicon sheet prepared from fused silicon in case of polycrystalline silicon, or plasma CVD employing silane gas etc. in case of amorphous silicon, or ion plating, ion beam deposition, vacuum evaporation, sputtering or electrophoresis in case of compound semiconductor.

The transparent conductive layer 204 serves as the upper electrode of the photovoltaic element. It can be composed, for example, of  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3\text{-SnO}_2$  (ITO),  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{Cd}_2\text{SnO}_4$ , a crystalline semiconductor layer doped with an impurity at a high concentration, or a translucent thin metal layer, and can be formed, for example, by resistance-heated evaporation, sputtering, spray coating, CVD or impurity diffusion.

On the transparent conductive layer, there can be provided a grid-shaped current-collecting electrode 205 for efficiently collecting the current. The current-collecting electrode 205 can be composed, for example, of conductive paste, prepared by dispersing finely powdered silver, gold, copper, nickel or carbon in polymer binder. The polymer binder can be composed, for example, of polyester resin, epoxy resin, acrylic resin, alkyd resin, polyvinyl acetate resin, rubber, urethane resin or phenolic resin. Also instead of the application of the conductive paste, the current-collecting electrode 205 can also be formed by sputtering, resistance-heated evaporation or CVD employing a mask pattern, evaporation of a uniform metal film followed by removal of unnecessary portions by etching direct formation of grid electrode pattern by photoactive CVD, plating with a negative mask of the grid-pattern electrode, or thin metal wires coated with hardened conductive paste.

Finally output terminals 206 are mounted on the conductive substrate and the current-collecting electrode, in order to collect the generated electric current. Said mounting on the conductive substrate is achieved by connecting a metal member, such as a copper tab, by spot welding or soldering, and that on the current-collecting electrode is achieved by connecting a metal member with conductive adhesive or solder 207. An insulator 208 is preferably provided in order to prevent shortcircuiting caused by eventual contact of the output terminal with the conductive substrate or the semiconductor layer, at the mounting on the current-collecting electrode.

The photovoltaic elements prepared by above-explained method are connected in serial or parallel manner according to the desired voltage or current. Also the photovoltaic elements may be formed in integrated manner on an insulated substrate, thereby providing a desired voltage or current.

#### Filler 104 at the Light Entrance Side

The filler 104 at the light entrance side is required to be transparent to the light absorbed by the photovoltaic element, and to be adhesive to the photovoltaic element 103 and to the hard film 105. It also has to be thermoplastic in order to fill the surface irregularities on the solar cell 103 constituting the photovoltaic element, thereby maintaining the smoothness of the hard film 105. Furthermore, in consideration of the protection of the photovoltaic element, it is preferably provided with scratch resistance and impact absorbing ability of a certain level. It can be composed, for example, of fluorinated resin, ethylene-vinyl acetate copolymer (EVA), polyvinyl butyral (PVB), silicone resin, epoxy resin or acrylic resin, but fluorinated resin is particularly preferable as the filler at the light entrance side, in consideration of the weather resistance. An example of such fluorinated resin is trifluorochloroethylene-vinyl copolymer.

The monomer to be copolymerized with trifluorochloroethylene can be a vinyl ether monomer or a vinyl ester monomer. The vinyl ether monomer can have a side chain such as methyl, ethyl, propyl, n-butyl, 2-butyl, tert-butyl, n-hexyl or cyclohexyl radical. The trifluorochloroethylene-vinyl copolymerization is known to achieve almost uniformly mixed copolymerization, regardless of the charge amounts of the monomers prior to the polymerization. Consequently, for ensuring flexibility in the copolymer, there is effectively employed a long alkyl radical at least equal to butyl radical or a side chain with steric hindrance such as cyclohexyl radical. If adhesive power to the photovoltaic element or to the surfacial film is required in addition to the flexibility, it is preferable to copolymerize a vinyl ester monomer. The side chain of the vinyl ester monomer can be an alkyl radical similar to that for the vinyl ether monomer.

Also effective is a mixture of polyfluorovinylidene and acrylic resin, with a preferred mixing ratio within a range from 1/9 to 4/6. A mixing ratio lower than 1/9 cannot exploit the weather resistance of polyfluorovinylidene or suffers from the lack of flexibility of acrylic resin, while a mixing ratio higher than 4/6, though providing sufficient weather resistance, requires a temperature of  $200^\circ\text{C}$  or higher for thermal lamination, thus leading to excessive crosslinking or deterioration by oxidation of the organic resin etc.

employed in the current-collecting electrode.

Also thermal lamination at 200°C or higher cannot provide sufficient adhesion to the photovoltaic element or to the surfacial film, even though thermoplasticity is present.

The acrylic resin to be employed in the present invention is not particularly limited, and examples of the main monomer constituting acrylic resin include methyl (meth)acrylate, ethyl (meth)acrylate, 2-propyl (meth)acrylate and n-propyl (meth)acrylate. If flexibility is required in the filler, there can be copolymerized butyl (meth)acrylate or 2-ethylhexyl (meth)acrylate. Copolymerization of styrene is also conceivable for reducing the moisture absorption of acrylic resin.

#### 10 Hard Film 105

The hard film to be employed in the present invention is not strictly defined, but it preferably has a thermal deformation temperature of 70°C or higher. The thermal deformation temperature can be defined, for example, by the deformation temperature under a load of 4.6 kg/cm<sup>2</sup> according to ASTM-D648-56. The properties required for the hard film 105 are transparency, weather resistance and scratch resistance. Examples of the preferred material therefor in the present invention include polyethylene, polystyrene, fluorinated resin, polycarbonate, acrylic resin cellulose resin, polyester and polyamide resin. More preferred is polycarbonate, polyethylene terephthalate belonging to polyester, or acrylic resin. In particular polycarbonate has a high mechanical strength and is also excellent in the weather resistance.

The film may be elongated for increasing the mechanical strength. Particularly a biaxially elongated film shows a tensile strength of 2 to 5 times of that of the unelongated film, also shows a significant increase in the initial modulus and the impact strength, and has a very high mechanical strength. Furthermore the transparency and the usable temperature range can be improved by such biaxial elongation, so that such elongated film is suitable as the covering material for the solar cell module.

#### 25 Trifluorochloroethylene-vinyl Copolymer 106 at the Outermost Surface

The monomer to be employed in the copolymer at the outermost surface of the present invention can be vinyl ether monomer or vinyl ester monomer. The vinyl ether monomer can be provided with a side chain such as methyl, ethyl, propyl, n-butyl, 2-butyl, tert-butyl, n-hexyl or cyclohexyl radical. Trifluorochloroethylene-vinyl copolymerization is known to achieve substantially uniformly mixed copolymerization regardless of the charging amounts of the monomers prior to polymerization.

It is already known to achieve crosslinking by copolymerizing a monomer having hydroxyl radical. Particularly preferred for such monomer having hydroxyl radical is 2-hydroxy (meth)acrylate.

The copolymer can be crosslinked with an isocyanate, melamine or an organic peroxide.

The isocyanates can be generally classified into aromatic ones and aliphatic ones. Those generally called free of yellow discoloration belong mostly to aliphatic ones, such as hexamethylene diisocyanate, isoholone diisocyanate, hydrogenated methylene bis(phenylisocyanate) etc. Aromatic isocyanate known to be free from yellow discoloration is triline diisocyanate.

The isocyanate mentioned above can be employed singly, but is often used in the state of an oligomer, called adduct or prepolymer, with a polyhydric alcohol. Such form can reduce the time required for crosslinking, as the crosslinking reaction is partly completed. Also it can avoid loss by evaporation even in case of crosslinking at a high temperature, because of a larger molecular weight. It is furthermore advantageous in terms of safety, as the larger molecular weight reduces the amount of vapor inhaled by human being or the amount absorbed from the skin.

The isocyanate is little used in the free form, in consideration of the pot life of the prepared mixture, but the activity of isocyanate can be blocked by a blocking agent.

For such blocking agent, there can be used phenols, alcohols, active methylenes, mercaptanes, acid amides, imides, amines, imidazoles, ureas, carbamates, imines, oximes and sulfite salts.

Examples of such phenol block agent include phenol, cresol, xylene, p-ethylphenol, o-isopropylphenol, thymol, p-naphthol, p-nitrophenol and p-chlorophenol. Examples of alcohol blocking agent include methanol, ethanol, propanol, butanol, ethylene glycol, methyl cellosolve, butyl cellosolve, methylcarbitol, benzyl alcohol, phenyl cellosolve, furfuryl alcohol and cyclohexanol.

Also examples of active methylenes include dimethyl malonate, diethyl malonate and ethyl acetoacetate, and those of mercaptanes include butylmercaptane, thiophenol and tertdodecylmercaptane.

Examples of acid amide include acetoanilide, acetoanilide, acetamide and benzamide, and those of imides include succinimide and maleimide.

Exâmples of amine include diphenylamine, phenylnaphthylamine, aniline and carbazole, and those of imidazole include imidazole and 2-ethylimidazole.

Examples of urea block agent include urea, thiourea and ethyleneurea, while those of carbamate include phenyl N-phenylcarbamate and 2-oxazolidone, while those of imine include ethylenimine. Examples of oxime include formaldoxime, acetaldoxime, methylethylketoxime and cyclohexanonoxime, and those of sulfite salt include sodium bisulfite and potassium bisulfite.

#### Inorganic Ultraviolet Absorber

Organic ultraviolet absorbers are well known, but it is difficult to expect the ultraviolet intercepting effect for a prolonged period, because of thermal decomposition or evaporation. For this reason an inorganic ultraviolet absorber is employed in the present invention. In comparison with the well known organic ultraviolet absorber such as benzophenone or benzotriazole, the inorganic one is featured by ultraviolet intercepting ability, long-term stability, heat resistance and safety. Examples of such inorganic ultraviolet absorber include zinc oxide, titanium oxide, yttrium oxide and cerium oxide.

In the following the present invention will be further clarified by examples thereof, but it is to be understood that the present invention is by no means limited by these examples.

#### Example 1

At first there will be explained the procedure for preparing an amorphous (non-monocrystalline) silicon (a-Si) solar cell, with reference to Fig. 2.

On a washed stainless steel substrate 201, there were formed, as the rear reflective layer 202, an Al layer (5000 Å thick) and a ZnO layer (5000 Å thick) in succession by sputtering. Subsequently there was formed a photoelectrically converting a-Si semiconductor layer 203 of a tandem configuration of n-layer (thickness 150 Å)/i-layer (thickness 4000 Å)/p-layer (thickness 100 Å)/n-layer (thickness 100 Å)/i-layer (thickness 800 Å)/p-layer (100 Å) by preparing n-conductive type (n-type) a-Si layers from a gaseous mixture of SiH<sub>4</sub>, PH<sub>3</sub> and H<sub>2</sub>, i-type a-Si layers from a gaseous mixture of SiH<sub>4</sub> and H<sub>2</sub>, and p-type microcrystalline  $\mu$ c-Si layers from a gaseous mixture of SiH<sub>4</sub>, BF<sub>3</sub> and H<sub>2</sub>, by plasma CVD. Subsequently an In<sub>2</sub>O<sub>3</sub> film of a thickness of 700 Å was formed as the transparent conductive layer 204, by resistance-heated evaporation of In in O<sub>2</sub> atmosphere. Finally the current-collecting grid electrode 205 was formed by screen printing of silver paste, whereby the photovoltaic element was completed. Each element had a size of 30 cm x 15 cm, and two elements were serially connected by adhesion with silver paste through copper tabs (thickness 50  $\mu$ m). An output terminal was mounted on the stainless steel substrate, utilizing a copper tab (thickness 50  $\mu$ m) and silver paste. An insulator 208 composed of polyamide resin (thickness 50  $\mu$ m) was provided as shown in Fig. 2, and the other output terminal was connected, utilizing a copper tab (thickness 50  $\mu$ m) and silver paste.

In the following there will be explained the outermost layer.

Paint was prepared by mixing 100 parts of trifluorochloroethylene-vinyl copolymer, 18 parts of block isocyanate, 1.5 parts of an inorganic ultraviolet absorber, 30 parts of fine silica powder and 80 parts of xylene. On a hard film, composed of polycarbonate (thickness 100  $\mu$ m; corona treated on both sides), the above-mentioned paint was applied by curtain coating, with a thickness of about 40  $\mu$ m, and was subsequently hardened at 120 °C for 30 minutes.

Thermal lamination was conducted with an aluminum plate (thickness 20 mm) provided with a heat source. On the aluminum plate heated to 150 °C, there were superposed, in succession, a galvarium steel plate 401 (thickness 0.3 mm); an EVA sheet (thickness 460  $\mu$ m) as the rear filler 402; a nylon film (thickness 70  $\mu$ m) as the rear insulator layer 403; an EVA sheet (thickness 460  $\mu$ m) as the rear filler 404; a photovoltaic element 405; a filler 406 (thickness 300  $\mu$ m); and polycarbonate/trifluorochloroethylene-vinyl copolymer 407, 408 laminated as explained above, and a heat-resistant silicone rubber sheet (thickness 3 mm) was placed thereon. An O-ring was employed as the seal, and the pressure inside the solar cell module was reduced to 10 mmHg with a vacuum pump. The surface hardness of the obtained solar cell module was 4H in pencil hardness.

The configuration of the covering materials is schematically shown in Fig. 4.

The solar cell module, prepared as explained above, was evaluated in the following tests:

(1) Conversion efficiency of solar cell:

There was conducted measurement of the conversion efficiency of the prepared solar cell module.

(2) Weather resistance:

The solar cell module was subjected in a Sunshine Weather Meter, to an accelerated weathering test

under repeated cycles of light irradiation and rain, and variation in the appearance and performance of solar cell were evaluated after 5000 hours. The result is represented as + if no variation was observed in the appearance, ± if variation was observed but was of a level not affecting the practical use, and - if the solar cell showed peeling or bending.

(3) Temperature/humidity cycle:

The solar cell module was subjected to 20 temperature/humidity cycles of -40 °C/1 hr and 85 °C/85 %RH for 4 hrs., and variation in the appearance after the test was observed. The results were evaluated in a similar manner as in the test (2).

(4) Scratch resistance test:

There was conducted the scratch test (UL standard) for testing whether the surface covering material had enough protecting ability against external scratching. The test was conducted, with a testing machine shown in Fig. 7, by moving a steel blade along the surface of the solar cell module, under a load of 907 g with a moving speed of 152.4 mm/sec. The solar cell module was subjected, after the scratch test, to a high-voltage insulation breakage test, and was regarded to have passed the scratch test if the module did not show a leak current. The scratch test was conducted on the copper tab, positioned highest in the solar cell module of the present invention.

The high-voltage insulation breakage test was conducted in the following manner. After the scratch test, the solar cell module was shortcircuited between the anode and the cathode, and was immersed in solution with an electrical conductivity of 3500  $\Omega$ cm or lower (containing 0.1% of a surfactant Triton X-100), with the output terminal of the module being maintained out of the solution. After the portion of the module, subjected to the scratch test, was rubbed for about 10 seconds, the cathode of a power source was immersed in the solution, and the another of the power source was connected to the output terminal of the module. A voltage of 2000 V was applied by the power source, and the module was regarded to have passed the test if the current was less than 0.5  $\mu$ A. In Table 1, the result is indicated by + or - respectively if the module passed or did not pass the test, and a case with poor reproducibility is indicated by +/-.

(5) Flame retarding property:

Flame of a lighter was maintained close to the surface covering material of the solar cell module for 30 seconds, and the material was evaluated as flame retarding if the flame extinguished spontaneously or if the material did not show any change after the lighter was separated. The result was evaluated as + in case of flame retarding, or - if the flame did not extinguish spontaneously.

## Example 2

A solar cell module was prepared in the same manner as in the Example 1, except that the inorganic ultraviolet absorber, added to trifluorochloroethylene-vinyl copolymer was replaced by 2-hydroxy-4-n-octoxybenzophenone which was an organic ultraviolet absorber. The obtained solar cell module has a pencil surface hardness of 4H.

## Example 3

A solar cell module was prepared in the same manner as in the Example 1, except that the inorganic ultraviolet absorber, added to trifluorochloroethylene-vinyl copolymer was replaced by 2-hydroxy-4-n-octoxybenzophenone which was an organic ultraviolet absorber and that the trifluorochloroethylene-vinyl copolymer (corresponding to 408) at the outermost surface was employed in an amount of 200 parts. The obtained solar cell module showed a pencil surface hardness of 2H.

## Example 4

A solar cell module was prepared in the same manner as in the Example 1, except that the inorganic ultraviolet absorber, added to trifluorochloroethylene-vinyl copolymer, was replaced by 2-hydroxy-4-n-octoxybenzophenone which was an organic ultraviolet absorber, that the trifluorochloroethylene-vinyl copolymer (corresponding to 408) at the outermost surface was employed in an amount of 200 parts and that PET (thickness 100  $\mu$ m) was employed as the hard film 407. The obtained solar cell module showed a pencil surface hardness of 2H.



Example 5

A solar cell module was prepared in the same manner as in the Example 1, except that the inorganic ultraviolet absorber, added to trifluorochloroethylene-vinyl copolymer, was replaced by 2-hydroxy-4-n-octoxybenzophenone which was an organic ultraviolet absorber, that the trifluorochloroethylene-vinyl copolymer (corresponding to 408) at the outermost surface was employed in an amount of 200 parts and that an acylic film (thickness 100  $\mu\text{m}$ ) was employed as the hard film 407. The obtained solar cell module showed a pencil surface hardness of 2H.

Example 6

A solar cell module was prepared in the same manner as in the Example 1, except that the inorganic ultraviolet absorber, added to trifluorochloroethylene-vinyl copolymer, was replaced by 2-hydroxy-4-n-octoxybenzophenone which was an organic ultraviolet absorber, that the trifluorochloroethylene-vinyl copolymer (corresponding to 408) at the outermost surface was employed in an amount of 200 parts and that an EVA (thickness 300  $\mu\text{m}$ ) was employed as the filler 406. The obtained solar cell module showed a pencil surface hardness of 2H.

Reference Example 1

A solar cell module of a configuration shown in Fig. 5 was prepared by superposing, on the light entrance side of a photovoltaic element 1005 prepared as explained before, an EVA sheet (thickness 460  $\mu\text{m}$ ; manufactured by Mobey) as the filler 1006 and an ETFE film (thickness 38  $\mu\text{m}$ ; Tefzel manufactured by duPont) as the outermost surface 1007, and also superposing a nylon film (thickness 70  $\mu\text{m}$ ; Dartec manufactured by duPont) as the rear insulator 1003; an EVA sheet (thickness 460  $\mu\text{m}$ ; manufactured by Mobey) as the rear filler 1002; and a galvarium steel plate 1001 (thickness 0.3 mm), and effecting lamination in the same manner as in the Example 1.

Reference Example 2

A solar cell module of a configuration shown in Fig. 6 was prepared in the same manner as in the Reference Example 1, except that the EVA filler at the light entrance side was composed of two EVA sheets 1107, 1106 (thickness 460  $\mu\text{m}$ ; manufactured by Mobey).

Reference Example 3

Lamination was conducted in the same manner as in the Example 1, employing, at the light entrance side of a photovoltaic element 1105 prepared as explained above, an EVA sheet (thickness 460  $\mu\text{m}$ ; manufactured by Mobey) as the filler (corresponding to 1106); a glass (Grane glass 230 manufactured by Crane Glass Co.) as a reinforcing layer 1207; an EVA sheet (thickness 460  $\mu\text{m}$ ; manufactured by Mobey) as the filler 1208; and an ETFE film (thickness 38  $\mu\text{m}$ ; Tefzel manufactured by duPont) as the outermost surface 1209.

The results of evaluations of the solar cell modules of the foregoing examples and reference examples are summarized in Table 1.

Table 1

	Initial conv. efficiency	Weather resistance	Temp/humidity cycle test	Scratch resistance	Flame retarding property
Example 1	8.0	+	+	+	+
Example 2	8.0	±	+	+	+
Example 3	8.0	±	+	+	+
Example 4	8.0	±	±	+	+
Example 5	8.0	±	+	+	+
Example 6	8.0	±	±	+	+
Reference Example 1	8.0	-	±	-	-
Reference Example 2	8.0	-	±	+/-	-
Reference Example 3	8.0	-	±	+	-

According to the present invention, the weather resistance can be improved by covering the surface of the solar cell module at the light entrance side with trifluorochloroethylene-vinyl copolymer. Also the deterioration of the covering material of the photovoltaic element by the ultraviolet light can be prevented by the addition of an inorganic ultraviolet absorber in said trifluorochloroethylene-vinyl copolymer. Also the weather resistance can be improved by the use of a filler consisting of fluorinated resin. Furthermore, scratch resistance and safety can be improved by the use of a hard film. A pencil surface hardness of 2H to 4H in the trifluorochloroethylene-vinyl copolymer can improve the scratch resistance, thereby protecting the module from scars and damages.

A surface covering material for the solar cell module, excellent in transparency, scratch resistance, weather resistance and flame retarding property, is obtained by covering the outermost surface with trifluorochloroethylene-vinyl copolymer, and employing a hard film 105 in the surface covering material under trifluorochloroethylene-vinyl copolymer. The hard film 105 and trifluorochloroethylene-vinyl copolymer 106 are laminated and adhered with filler 104 to the photovoltaic element 103.

### Claims

1. A solar cell module provided with a photovoltaic element having at least a photoactive semiconductor layer as the photoelectric converting member, comprising trifluorochloroethylene-vinyl copolymer at least at the outermost surface of the surface covering material at the light entrance side.
2. A solar cell module according to claim 1, wherein said photoactive semiconductor layer is composed of a non-monocrystalline semiconductor film.
3. A solar cell module according to claim 2, wherein said non-monocrystalline semiconductor film is composed of amorphous silicon.
4. A solar cell module according to claim 1, wherein said surface covering material is composed of trifluorochloroethylene-vinyl copolymer laminated on a hard film and adhered with a filler.
5. A solar cell module according to claim 4, wherein said hard film is composed of a resinous material with a thermal deformation temperature of 70 °C or higher.
6. A solar cell module according to claim 4, wherein said hard film is composed of acrylic resin, polycarbonate resin or polyester resin.
7. A solar cell module according to claim 4, wherein said filler is composed of fluorinated resin.
8. A solar cell module according to claim 1, wherein said trifluorochloroethylene-vinyl copolymer has a pencil surface hardness within a range of 2H to 4H.

9. A solar cell module according to claim 1, wherein said trifluorochloroethylene-vinyl copolymer is added with an ultraviolet absorber consisting of an inorganic compound.
10. A solar cell module according to claim 1, wherein said ultraviolet absorber is composed of titanium oxide, yttrium oxide or cesium oxide.
11. A solar cell module according to claim 1, wherein said trifluorochloroethylene-vinyl copolymer contains an isocyanate.
12. A solar cell module according to claim 1, wherein said trifluorochloroethylene-vinyl copolymer contains a blocking agent.

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FIG. 1

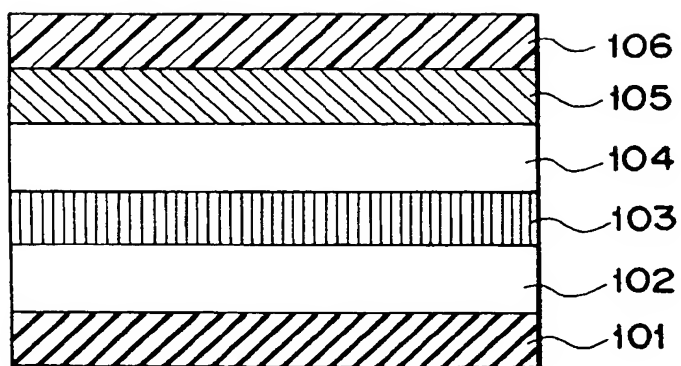


FIG. 2

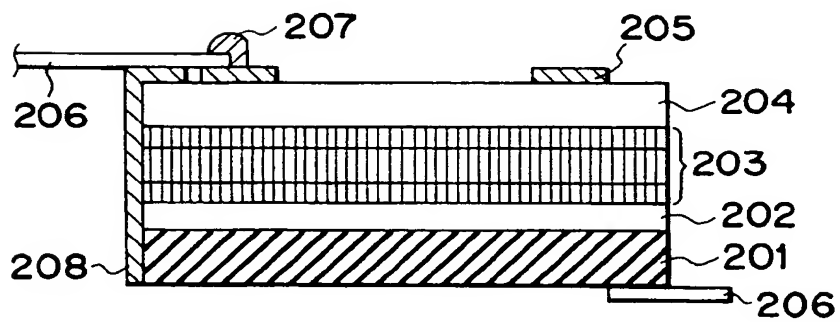


FIG. 3

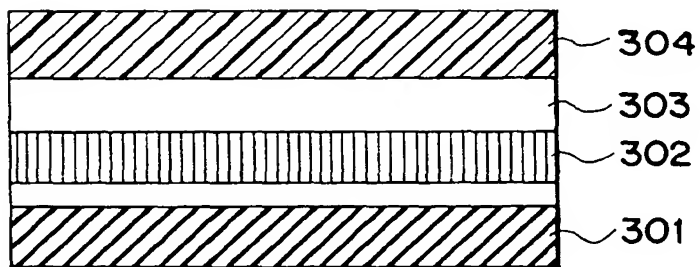


FIG. 4

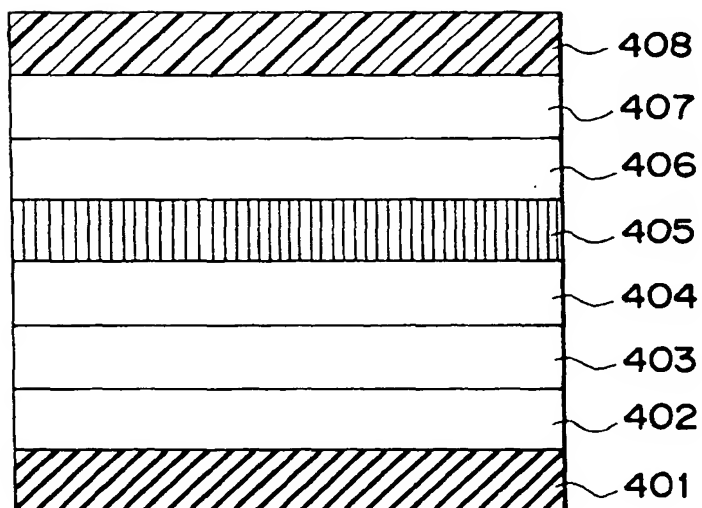


FIG. 5

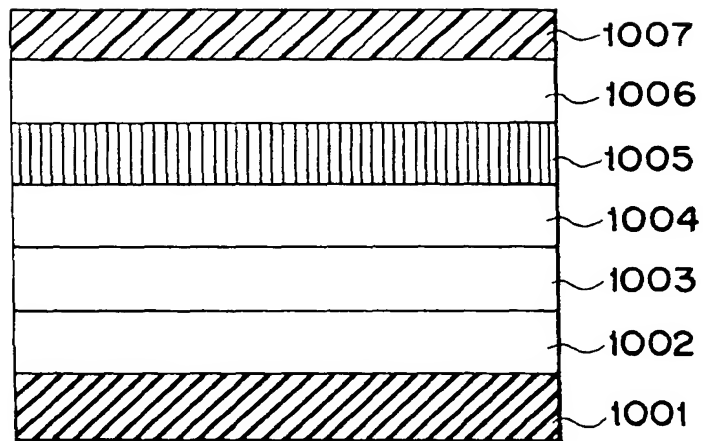


FIG. 6

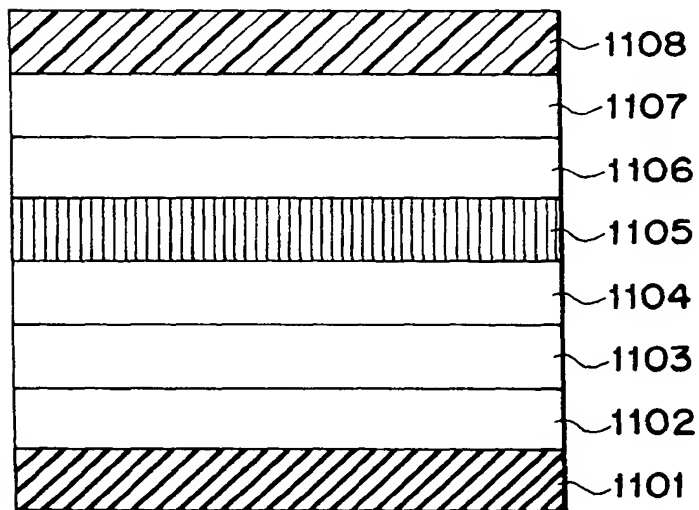
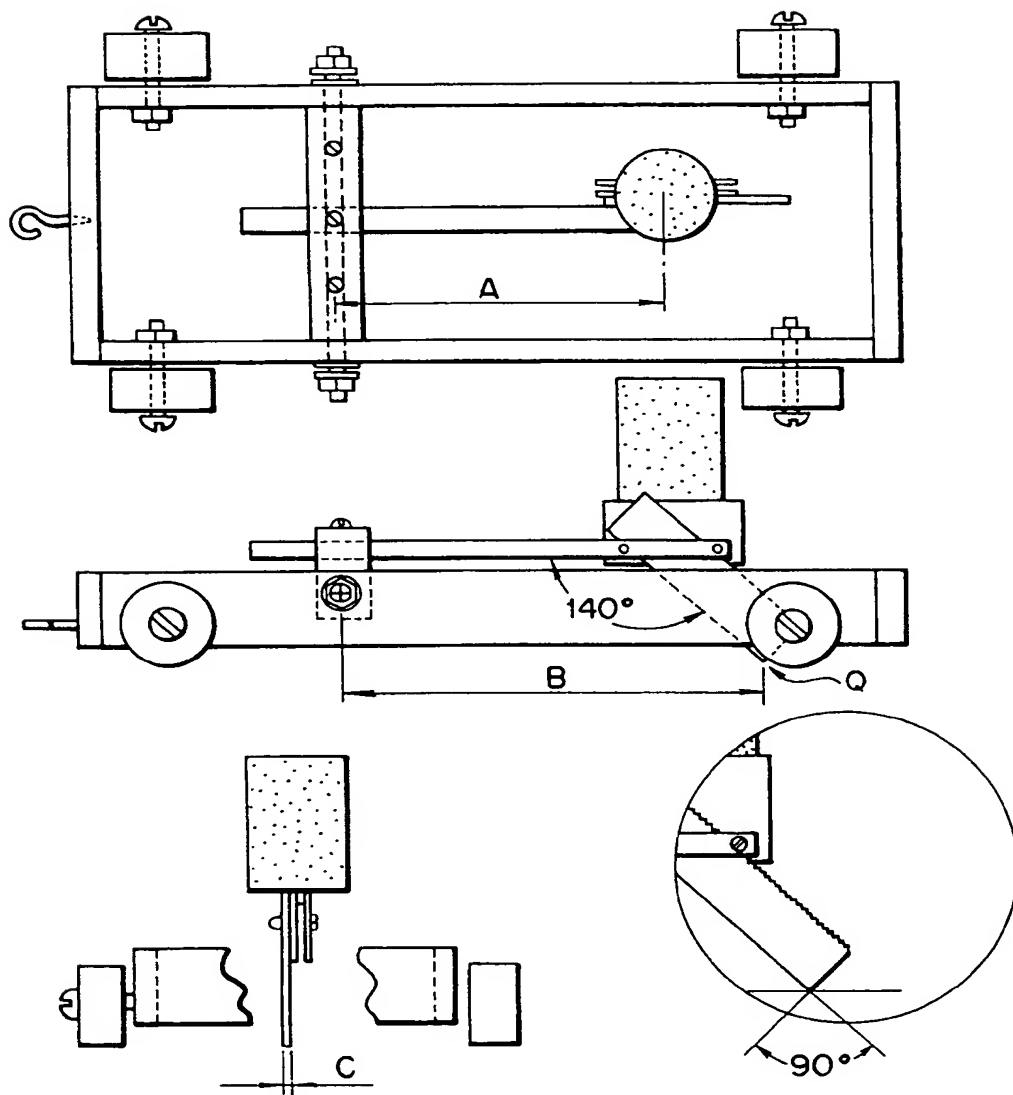


FIG. 7

SCRATCH TESTER





European Patent  
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## EUROPEAN SEARCH REPORT

Application Number  
EP 94 10 9043

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	FR-A-2 539 419 (PHOTOWATT INTERNATIONAL) * claims * ---	1,4,9	H01L31/048 H01L31/0216
A	DATABASE WPI Week 8114, Derwent Publications Ltd., London, GB; AN 81-25019D & SU-A-750 575 (KONDRATEVA ET AL) * abstract * ---	1	
A	DE-A-27 51 517 (LICENTIA PATENT VERWALTUNG) * the whole document * ---	1,4,5	
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 99 (E-493) 27 March 1987 & JP-A-61 251 176 (TOPPAN PRINTING CO LTD) 8 November 1986 * abstract * ---	1,4	
A	PATENT ABSTRACTS OF JAPAN vol. 6, no. 243 (E-145) 2 December 1982 & JP-A-57 143 872 (NIHON ITA GLASS KK) 6 September 1982 * abstract * ---	1	TECHNICAL FIELDS SEARCHED (Int.Cl.5) H01L
A,D	PATENT ABSTRACTS OF JAPAN vol. 8, no. 155 (E-256) 19 July 1984 & JP-A-59 056 776 (NITTO DENKI KOGYO KK) 2 April 1984 * abstract * -----	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 September 1994	Examiner Lina, F
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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